Key Engineering Materials Vols. 471-472 (2011) pp 397-402

doi:10.4028/www.scientific.net/KEM.471-472.397

The Study of Biodegradable Thermoplastics Sago Starch

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Keywords: Sago starch, Biodegradable, Thermoplastic Starch (TPS)

Abstract. The motivation of this work is to lessen the dependence on non-degradable plastic packaging which can lead to waste disposal problems. In this paper, the alternative biodegradable material developed by using local available sago starch in the present of biodegradable glycerol as plasticizer, as well as a set of composition added with citric acid as co-plasticizer is reported. Starch was added with 15-30 w/w% of glycerol to prepare workable bioplastics. The samples were characterized by Thermal Gravimetric Analysis (TGA), Fourier Transform Infrared (FTIR) and tested for mechanical properties. The results reveale that, the tensile strength of the bioplastic is increasing with the increasing of glycerol until the optimum amount of 30 w/w%. The similar trend is also observed upon the addition of the citric acid. The decrease of the strength after the optimum point, however is obvious in the specimens with the addition of citric acid which is about 50% lower than the specimen without citric acid.

Introduction

It is undeniable, although conventional plastic is good, but it still has some limitations. As a fact, many researchers emphasized that plastic waste leads to environmental problems. According to Santos [1], conventional plastic offer bad consequences for the environment due to common polyolefins which have very poor degradation rate. This fact is supported by Fischer [2], who claimed that high cost is needed to store the non-degradable plastic while burning it will produce carbon dioxide (CO_2) which leads to green house effect. For the stated reasons, it can be concluded that the usage of conventional thermoplastic make the environmental problem become crucial [1-2].

Thermoplastic starch has been introduced as an attempt to overcome these drawbacks. Thermoplastic starch (TPS) is a homogenous thermoplastic substance made from native starch. After undergoes several processes, thermoplastic starch may transform from semi-crystalline into amorphous polymeric material. It should be noted that, thermoplastic starch is practical to be used due to it has starch content more than 70% and with the use of specific plasticizing solvents, materials with good properties and biodegradability can be produced.

Sago starch is a true wonder of nature and known as the most important raw material due to its low cost, availability as a renewable resource, biodegradable and the harmless degradation products [3]. Sago starch can be processed into thermoplastic starch under the action of temperature and shearing action. Plasticizer need to be used while processing, because of the low decomposition temperature of the granular starch [4].

This work is undertaken to explore the potential of sago starch as natural sources for the production of biodegradable thermoplastic. The objectives of this study are to optimize the process condition in order to produce high performance materials and to study the effect of co-plasticizer on the mechanical and thermal properties of the thermoplastic starch. Further, tensile fracture specimen was viewed under scanning electron microscope for morphological analysis.

Experimental Method

Materials. Sago starch powder (25% amylose) was purchased from Hup Seng Heng Sdn Bhd, Malaysia, glycerol (95% purity) with density of about 1.261 g/cm³ and citric acid were supplied by Merck.

Fabrication Process. In this experiment there were two compositions prepared. First is a mixture of starch and glycerol. Secondly, a blend of starch powder, glycerol and citric acid. Basically, the starch was plasticized with glycerol (95% purity) while citric acid was used as a co-plasticizer. Material ratios were stated specifically in the Table 1 and Table 2 below and glycerol-mono-stearate was added as a lubricant.

Table 1 Thermoplastic starch with different glycerol's content.

Sample	Glycerol (w/w%)
G1	15
G2	20
G3	30
G4	40

Table 2 TPS with the addition of citric acid

Sample	Glycerol (w/w%)	Citric Acid (w/w%)
C1	30	10
C2	30	20
C3	30	30
C4	30	40

Thermoplastic starch (TPS) was produced in a three distinct steps. The materials were weighted by using digital lab weight scales and mixed using stirrer. The obtained mixture was stored for 24 hrs in an air tight polyethylene bags at room temperature before processed with a twin screw extruder Thermo HAAKE Rheomix 600 which is used for melt blending purposes at a temperature 130°C, 100 rpm. Then, the extrudate was granulated and stored under controlled conditions for 48 hours. Finally, the granulates were injection molded according to the parameter in Table 3:

Table 3 Injection moulding parameters

Injection Pressure	Injection rate	Holding pressure	Temperature Z1	Temperature Z2	Temperature Z3	Temperature Z4	Temperature Z5
1400 bar	50 cm^3/s	600 bar	110°C	115°C	120°C	125°C	150°C

Results and Discussion

Tensile Strength. The effect of adding glycerol on the tensile strength of TPS is shown in the Fig. 1. It should be noted that**,** TPS with less than 20w/w% glycerol content had low tensile strength and was not considered for further studies. Increasing the concentration up to 30w/w% resulted in a maximum tensile strength value and also provides flexible product. The tensile strength decreased as the increased of glycerol up to 40%. Thus, 30% glycerol provided the maximum tensile strength and was used for subsequent studies. A primary concern, at low concentrations of glycerol (<15w/w %), is that, there is not enough plasticising effect and the starch molecules become brittle (Ma, 2009). At concentrations above 30w/w%, the plasticising effect is too pronounced and makes the starch molecules move easily. Thus, in this project the optimum amount of glycerol to be added is 30w/w% due to it leads to high strength (23.060 MPa).

Furthermore, addition of citric acid to the mixture improved the tensile strength. Concentration of citric acid less than 20w/w% however, provide relatively low improvement while concentration at 30w/w% gives high molecular weight of the starch and provides better interactions between molecules and result in better tensile strength compared to mixing starch with glycerol alone. As consequences, 30w/w% addition of citric acid into TPS gave an optimum value of tensile strength which is 24.766 MPa.

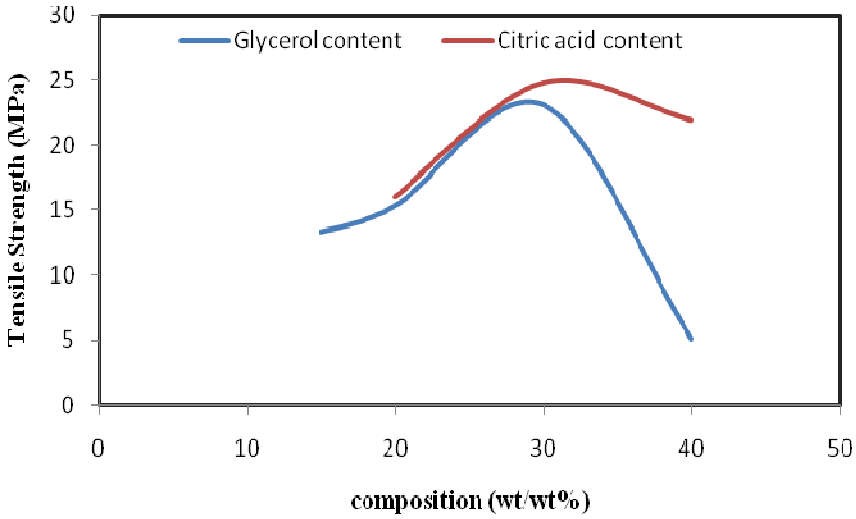


Fig. 1 Tensile strength vs. % Composition

Fourier Transform Infrared Spectroscopy (FTIR) Analysis. The analysis of Fourier Transform Infrared Spectroscopy (FTIR) spectra of the blends enabled the hydrogen bond interaction to be identified. According to Yang (2006), lower wave number results in stronger interaction of hydrogen bond. Fig. 2 shows that the characteristic peaks 1080 cm^{-1} and 1157 cm^{-1} indicate the C-O bond stretching of C-O-H group [6]. The peak 1080 cm^{-1} was shifted to 1078 cm^{-1} and from 1150 cm^{-1} to 1148 cm^{-1} which means the OH group of starch took part in the hydrogen bond formation. Another two peaks at 999 cm^{-1} and 1020 cm^{-1} are attributed to C-O bond stretching of C-O-C group [6]. The peaks were shifted from 998 cm^{-1} to 995 cm^{-1} and 1018 cm^{-1} to 1016 cm^{-1} respectively. In sum, the FTIR test for composition 1 is clearly showed that glycerol could form a more stable hydrogen bond.

In addition, Fig. 3 illustrates the FTIR result for the effect of acid citric content (composition 2). The change of the peaks position from 1709 cm^{-1} in pure citric acid to 1729 cm^{-2} in thermoplastic starch (TPS) illustrates that the ester bond existed. Peak at 1729 cm^{-1} reflect the increase of ester bonds. The peak's height increased as the citric acid content increased. It is noted that, the citric acid is more capable in disrupting inter and intra molecular hydrogen bonds.

Scanning Electron Microscopy (SEM). Stable hydrogen bond was formed between plasticizer and starch by the analysis of FTIR spectra. The morphology of sago starch granules and the extruded TPS were shown in Figs 4. Fig. 4(a) illustrates that the sago starch has an amorphous homogeneous matrix surrounds with predominant granular domains. TPS plasticized by 20% of glycerol result in a less coarse granules compared to native sago starch. This occurred due to starch granule has fused into homogeneous phase as revealed in Fig. 4(b) which led to some empty space in the TPS. Furthermore, plasticized TPS with glycerol had a clear and smooth surface as seen in Fig. 4(c) for the compositions of 30w/w%, and vice versa for 40w/w% plasticization. It should be noted that, as plasticizer content increases, melt viscosity decreases which made the plasticization of starch difficult, due to the reduction in shear during processing [6]. As a conclusion, glycerol with 30w/w% concentration is the most preferable composition to be used in the further studies.

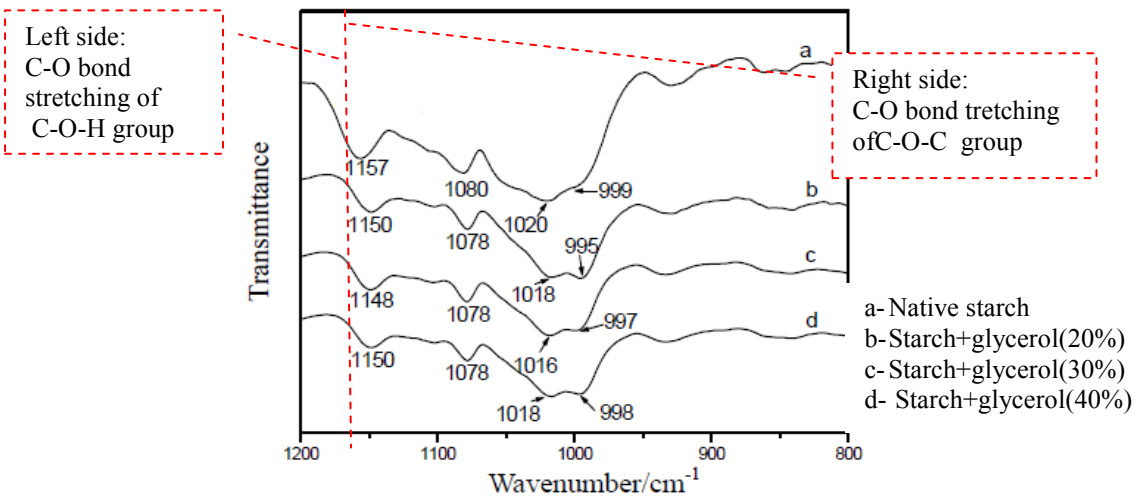


Fig. 2 FTIR shows the effect of glycerol content on TPS

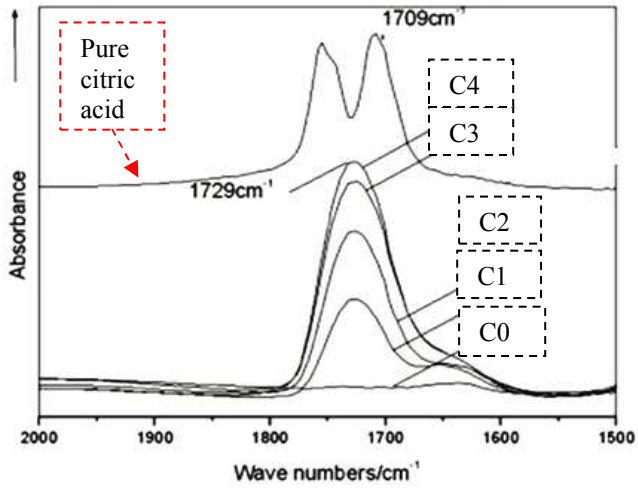
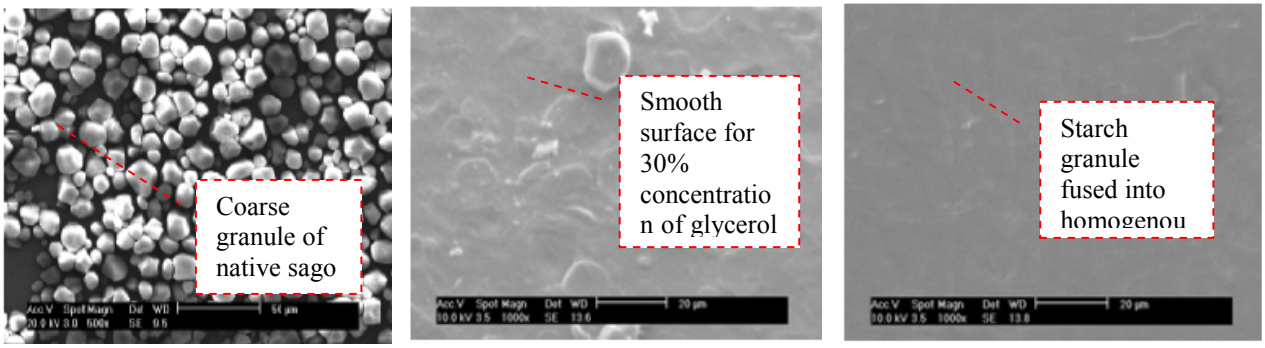


Fig. 3 FTIR shows the effect of acid citric content on TPS



(a) (b) (c)

Fig. 4 (a) SEM micrograph of sago starch (b) SEM micrograph of 20w/w% Glycerol (c) SEM micrograph of 30w/w% Glycerol

Thermo Gravimetric Analysis (TGA). Generally, TGA is a testing that is performed in order to determine the changes in weight with temperature. Fig. 5 show the thermogravimetric curves of TPS with and without addition of citric acid. It is noted that, the weight loss below 100°C was

mainly caused by water evaporation, while above 100°C are referring to evaporation of water and other plasticizers and thermal decomposition of the starch. Therefore, the differences in the onset temperatures of starch thermal decomposition and weight loss at onset temperature were mainly due to the type and content of the plasticizers [6]. There is only one weight loss step on the TG curve of TPS without citric acid, but two steps on the curves of TPS with citric acid. Specifically, the first weight loss step that started from 150 °C may be due to the heat decomposition of the residual citric acid in TPS with citric acid.

The second step was mainly caused by the thermal decomposition of the starch chains [6]. The onset temperatures of the second weight loss steps are strongly related to the interactions between plasticizers and the starch. TPS with citric acid had higher onset temperature and lower mass loss than TPS without citric acid. This indicated that the presence of citric acid is significant in increased the binding of plasticizers to starch. In other words, the bonding between the citric acid and starch is stronger than that between glycerol and starch.

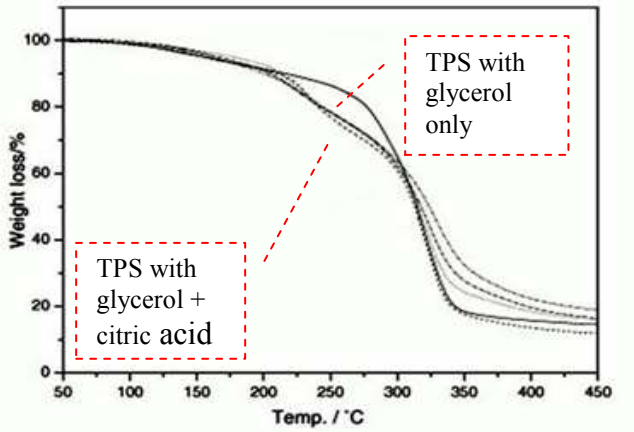


Fig. 5 TGA for TPS with and without citric acid

Summary

- Fourier Transform Infrared Spectroscopy (FTIR) analysis showed that glycerol could form a stable hydrogen bond while the addition of citric acid could disrupt inter and intra molecular hydrogen bond effectively.
- Scanning Electron Microscopy (SEM) proved that thermoplastic starch (TPS) plasticized with 30% glycerol result in fined granule compared to native starch had a clear and smooth surface.
- Optimum tensile strength for composition 1 (starch+glycerol) was 23.060 MPa while for composition 2 (starch+glycerol+citric acid) was 24.766 MPa.
- Thermo Gravimetric (TGA) analysis showed that the residual weight percentage of composition 2 increased with citric acid content.

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